

# Magnetic studies of multi-walled carbon nanotube mats: Evidence for the paramagnetic Meissner effect

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We report magnetic measurements up to 1200 K on multi-walled carbon nanotube mats using Quantum Design vibrating sample magnetometer. Extensive magnetic data consistently show two ferromagnetic-like transitions at about 1000 K and 1275 K, respectively. The lower transition at about 1000 K is associated with an Fe impurity phase and its saturation magnetization is in quantitative agreement with the Fe concentration measured by an inductively coupled plasma mass spectrometer. On the other hand, the saturation magnetization for the higher transition phase ( $\geq 1.0$  emu/g) is about four orders of magnitude larger than that expected from the measured concentration of Co or CoFe, which has a high enough Curie temperature to explain this high transition. We show that this transition at about 1275 K is not consistent with a magnetic proximity effect of Fe-carbon systems and ferromagnetism of any carbon-based materials or magnetic impurities but with the paramagnetic Meissner effect due to the existence of  $\pi$  Josephson junctions in a granular superconductor.

There are reports of weak ferromagnetism in graphite and carbon-based materials well above room temperature [1, 2, 3, 4, 5], as well as a theoretical prediction of a ferromagnetic instability in graphene sheets [6]. It is unclear whether the high-temperature ferromagnetism is intrinsic or simply caused by contamination of magnetic impurities [7]. There are also several reports of high-temperature superconductivity in carbon films [8, 9], carbon nanotubes [10, 11, 12], and graphite [2, 3, 13]. Gonzalez *et al.* [14] show that both high-temperature ferromagnetic and  $p$ -wave superconducting instabilities can occur in defective regions of graphite, where topological disorder enhances the density of states. Schrieffer [15] predicts ultra-high temperature superconductivity at a quantum critical point where ferromagnetic fluctuations are the strongest.

Here we report magnetic measurements up to 1200 K on multi-walled carbon nanotube mats. our extensive magnetic data consistently show two ferromagnetic-like transitions at about 1000 K and 1275 K, respectively. We show that the lower transition transition at about 1000 K is associated with an Fe impurity phase while the transition at about 1275 K is not consistent with a magnetic proximity effect in Fe-carbon systems and ferromagnetism of any carbon-based materials or magnetic impurities but with the paramagnetic Meissner effect due to the existence of  $\pi$  Josephson junctions in a granular superconductor.

Purified multi-walled nanotube (MWNT) mat samples are obtained from SES Research of Houston. Two different samples (Lot #'s RS0656 and RS0657) were prepared by chemical vapor deposition using an iron catalyst. By burning off carbon-based materials in air, we find the weights of the residuals to be 2.25% and 1.725% for RS0656 and RS0657, respectively. On the assumption that the residual contains  $\text{Fe}_2\text{O}_3$ ,  $\text{Co}_m\text{O}_n$ , and  $\text{Ni}_p\text{O}_q$  (where  $m$ ,  $n$ ,  $p$ , and  $q$  are integers), we determine the relative metal concentrations of the residual using a Perkin-Elmer Elan-DRCe inductively coupled

plasma mass spectrometer (ICP-MS). Since the Co and Ni concentrations are negligibly small, the relative metal contents are nearly independent of the valences of Co and Ni we choose for their oxides. From the ICP-MS result and the weight of the residual, we obtain the metal-based magnetic impurity concentrations (ppm in weight) for RS0656: Fe = 5342.4, Co = 0.5, Ni = 13.7; and for RS0657: Fe = 6940.8, Co = 36.1, Ni = 20.5.

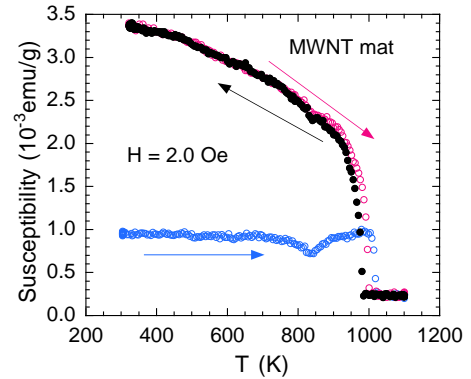


FIG. 1: Temperature dependence of the susceptibility in a field of 2 Oe for a virgin MWNT mat sample (RS0657).

Magnetization was measured by a Quantum Design vibrating sample magnetometer (VSM). The absolute uncertainty of the temperature is less than 10 K, as checked by the Curie temperatures of both Ni and Fe. Fig. 1 shows the temperature dependence of the susceptibility in a field of 2 Oe for a virgin MWNT mat sample (RS0657). This virgin sample was inserted into the sample chamber without going through the linear motor used for vibrating the sample. A 2 Oe field (using the ultra-low field option) was then applied after the sample was inserted. From the warming data, we clearly see a dip feature at about 833 K, which is caused by the competing effect of the ferrimagnetic transition at about 860 K for the  $\text{Fe}_3\text{O}_4$  impurity phase and the decomposition of

$\text{Fe}_3\text{O}_4$  into the higher Curie temperature  $\alpha$ -Fe phase due to the high vacuum inside the sample chamber (better than  $9 \times 10^{-6}$  torr). From the subsequent cooling and warming data, we see that the Curie temperature ( $T_C$ ) of the Fe impurity is about 1000 K, which is lower than that (1047 K) for the bulk pure  $\alpha$ -Fe. This is possibly due to the doping of carbon into Fe, which can significantly lower the  $T_C$  value [16].

From Figure 1, it is also apparent that the substantial low-field susceptibility (about  $2.3 \times 10^{-4}$  emu/g) persists up to 1100 K, which could arise from ferromagnetism of the Co or CoFe impurity phase. It is interesting that the same magnitude of the paramagnetic susceptibility is also seen in sample RS0656 where the Co concentration is only 0.5 ppm. The concentration of Co (0.5 ppm) or CoFe (about 1 ppm) is *over three orders of magnitude* too small to explain the measured paramagnetic susceptibility. Therefore, the observed large paramagnetic susceptibility well above the  $T_C$  of the Fe impurity phase should originate from ferromagnetism of a carbon-based phase or from the paramagnetic Meissner effect due to superconductivity.

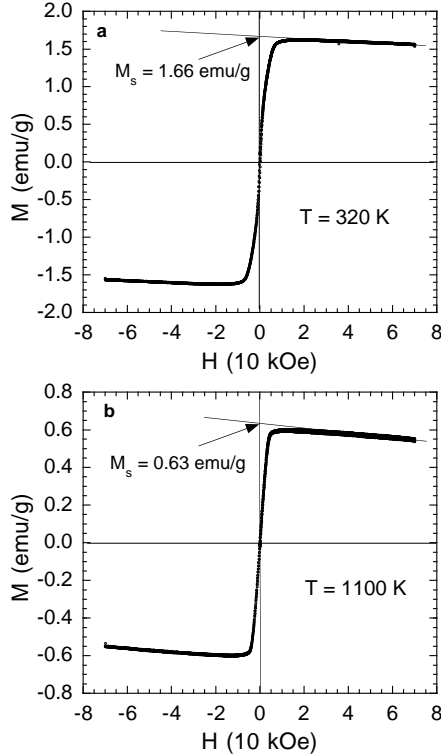


FIG. 2: Magnetic hysteresis loops at 320 K (a) and 1100 K (b) for sample RS0657. The coercivity  $H_C$  is about 140 Oe at 320 K and negligibly small at 1100 K.

In Figure 2, we plot the magnetic hysteresis loops at 320 K and 1100 K, which were measured after the above low-field measurements. The coercivity  $H_c$  is about 140 Oe at 320 K while it becomes negligibly small at 1100 K. The saturation magnetizations  $M_s$  at 320 K and 1100 K

are 1.66 emu/g and 0.63 emu/g, respectively. It is clear that the saturation magnetization at 1100 K is substantial, indicating a second magnetic transition above 1100 K. This second ultra-high temperature ferromagnetic-like (UHTFL) phase cannot be associated with the Co (or CoFe) impurity whose concentration is only 36.1 ppm (or 72 ppm) in this sample. Such a small Co or CoFe impurity concentration can contribute a saturation magnetization of  $< 1.0 \times 10^{-2}$  emu/g (see [17]), which is about two orders of magnitude smaller than the measured value (0.63 emu/g). For sample RS0656, which contains 5342.4 ppm Fe impurity and 0.5 ppm Co impurity, the  $M_s$  values at 320 K and 1100 K are 1.60 emu/g and 0.59 emu/g, respectively, which are very similar to those for sample RS0657. The measured  $M_s$  at 1100 K for sample RS0656 is about four orders of magnitude larger than the value expected from the measured Co or CoFe impurity concentration. This definitively excludes the Co or CoFe impurity from being the origin of the UHTFL phase.

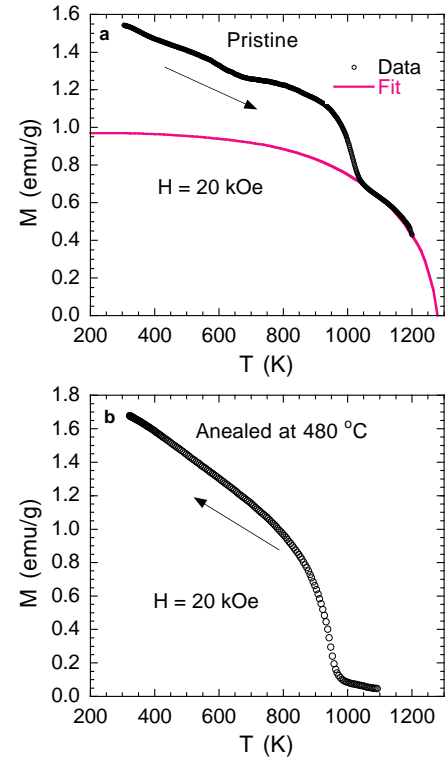


FIG. 3: a) Temperature dependence of the magnetization in a field of 20 kOe for a virgin MWNT mat sample (RS0657). The temperature dependence of the magnetization in 20 kOe should be similar to that of the saturation magnetization ( $M_s$ ). The solid line is a fit using the curve of  $M_s(T)/M_s(0)$  versus  $T/T_C$  for Ni, appropriately scaled to  $T_C = 1275$  K. b) Temperature dependence of the magnetization in a field of 20 kOe for a thermally annealed sample of RS0657. This sample was annealed in air at 480 °C for about 5 minutes.

Since the magnetization in 20 kOe is close to the saturation magnetization (see Fig. 2), the temperature dependence of the saturation magnetization can be simulated

by the temperature dependence of the magnetization in 20 kOe. In Fig. 3a, we plot the temperature dependence of the magnetization in a field of 20 kOe for another virgin sample of RS0657. One can clearly see that the magnetization above the Curie temperature of the Fe impurity phase is large up to 1200 K, implying that the transition temperature of the UHTFL phase is higher than 1200 K. If we assume that the curve of  $M_s(T)/M_s(0)$  versus  $T/T_C$  for this UHTFL phase is the same as that for Ni (see the solid line), we find  $T_C$  and  $M_s(0)$  to be 1275 K and 0.97 emu/g respectively. Then the saturation magnetization at 320 K contributed from the Fe impurity phase is 0.57 emu/g.

In Figure 3b, we show the temperature dependence of the magnetization in a field of 20 kOe for a thermally annealed sample of RS0657. This sample was annealed in air at 480 °C for about 5 minutes and its mass was measured about 1 hour after it was cooled down to room temperature. The mass of the annealed sample was found to be smaller than that of the pristine sample by 2%. This mass decrease may be due to the removal of amorphous carbon and/or the outershells of MWNTs. The data were taken after an  $M$ - $H$  loop was measured at 1100 K so that all the Fe oxides had been converted to  $\alpha$ -Fe in such a high vacuum and temperature. It is remarkable that the magnetization at 1100 K is reduced by one order of magnitude compared with that for the pristine sample (see Fig. 3a) while the magnetization at 320 K increases by 10%.

Figure 4 shows the temperature dependence of the magnetization in a field of 20 kOe for the residual of sample RS0657, which was obtained by burning off carbon-based materials in air at 550 °C for about 10 minutes. The data were similarly taken after an  $M$ - $H$  loop was measured at 1100 K. The specific magnetization was calculated using the mass of the pristine MWNT mat sample. As indicated by the arrow, the ferromagnetic transition temperature is about 1037 K which is the same as the  $T_C$  of  $\alpha$ -Fe if one considers a thermal lag of about 10 K. It is striking that the magnetization of the residual at 320 K is three times smaller than that for the annealed sample containing MWNT mats (Fig. 3b). This implies a giant enhancement of the magnetization of the Fe impurity due to the proximity to MWNTs. Moreover, we have independently shown that the Fe-based impurity phase in virgin samples is  $\text{Fe}_3\text{O}_4$ . If only this  $\text{Fe}_3\text{O}_4$  impurity phase is magnetic, the upper limit of the room-temperature  $M_s$  value for sample RS0656 is calculated to be 0.68 emu/g using the room-temperature  $M_s$  value (92 emu/g) of the bulk  $\text{Fe}_3\text{O}_4$  and the inferred  $\text{Fe}_3\text{O}_4$  concentration (7372.5 ppm) from the metal-based Fe concentration (5342.4 ppm). This upper limit of the room-temperature  $M_s$  value due to the  $\text{Fe}_3\text{O}_4$  impurity phase is about one third of the measured value (1.60 emu/g). It is interesting that such a giant enhancement of the moment was also observed in one of the Canyon Diablo graphite nodule samples (see the results for sample 1.1

of Ref. [18]).

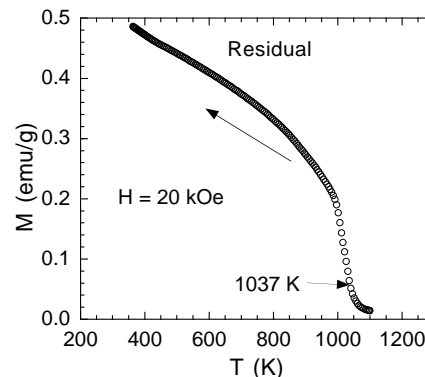


FIG. 4: Temperature dependence of the magnetization in a field of 20 kOe for the residual of sample RS0657, which was obtained by burning off carbon-based materials in air at 550 °C for about 10 minutes.

From  $M$ - $H$  loop measurements of the residual, we find the saturation magnetizations at 320 K and 1100 K to be 0.52 emu/g and  $4.5 \times 10^{-3}$  emu/g, respectively. The  $M_s$  value of the  $\alpha$ -Fe impurity at 320 K inferred from the data of the residual is in excellent agreement with that (0.57 emu/g) inferred from the data of the pristine sample (Fig. 3a). If we calculate  $M_s$  using the mass of the Fe impurity in the residual, we find  $M_s$  to be 74.9 emu per gram of Fe in agreement with the value used in Ref. [18]. Our magnetic measurements on  $\text{Fe}_3\text{O}_4$  nanoparticles with an average diameter of 40-60 nm also show that  $M_s = 77.0$  emu per gram of Fe at 320 K after the decomposition of  $\text{Fe}_3\text{O}_4$  into Fe through thermal cycling up to 1100 K in high vacuum. This implies that the  $M_s$  value of Fe nanoparticles is significantly smaller than the bulk value ( $\sim 200$  emu/g), which could be caused by spin disorder on the surface of nanoparticles [19]. Moreover, the measured  $M_s$  value at 1100 K ( $4.5 \times 10^{-3}$  emu/g) is nearly the same as the  $M_s$  value at 1100 K ( $4.5 \times 10^{-3}$  emu/g) expected from the measured Co impurity concentration (36.1 ppm) [17]. Such excellent consistencies between the magnetic data of the residual and the ICP-MS results further demonstrate that the UHTFL phase seen in Fig. 1, Fig. 2b, and Fig. 3a is not associated with any magnetic impurity phase.

Now we discuss the origin of the UHTFL phase and the giant enhancement of the magnetization of the Fe impurity. The UHTFL phase and related giant moment enhancement of the Fe impurity could arise from magnetic proximity between Fe nanoparticles and MWNTs [18]. However, this picture cannot consistently explain the results shown in Fig. 3 and Fig. 4. Annealing the sample in 480 °C may destroy the proximity effect so that the UHTFL phase is converted to the isolated Fe impurity phase. The converted Fe phase should have a much smaller saturation magnetization than the coupled Fe-MWNT phase which contains extra proximity-induced moments in MWNTs. The fact that no reduction of the

$M_s$  value at 320 K is found in the annealed sample argues against this interpretation. Further, the observed 90% decrease in the saturation magnetization at 1100 K implies that the coupled Fe-MWNT phase in the annealed sample would have been destroyed by about 90% so that the  $M_s$  value at 320 K for the annealed sample would be slightly larger than that for the residual sample with no proximity effect. However, the  $M_s$  value at 320 K for the annealed sample (Fig. 3b) is over three times larger than that for the residual sample (Fig. 4), which makes the above interpretation very unlikely. Another possibility is that the UHTFL phase is related to ferromagnetism of an unknown carbon-based material (e.g., amorphous carbon). Such a high Curie temperature (1275 K) for a carbon-based material would be very remarkable. Annealing the sample in air up to 480 °C removes amorphous carbon, and the observed 90% decrease in the saturation magnetization at 1100 K appears to indicate that the UHTFL phase could be related to amorphous carbon. However, if this interpretation were correct, the  $M_s$  value at 320 K would also be reduced to about 0.6 emu/g, in sharp contrast to the measured value (1.7 emu/g). A third possibility is that MWNTs are ferromagnetic with an ultra-high Curie temperature (1275 K). This is also very unlikely unless, per Fig. 3b, the annealing procedure causes the Curie temperature of the MWNTs to be exactly the same as that of the Fe impurity phase.

It is clear that one cannot consistently explain our present data based on the magnetic proximity effect and the ultra-high temperature ferromagnetism of unknown carbon-based phases, MWNTs, or magnetic impurities. Alternatively, if MWNTs are superconducting, a MWNT mat should be a granular superconductor. The existence of magnetic impurities in the Josephson network should lead to the formation of  $\pi$  junctions with a negative Josephson coupling energy  $J$  [20]. If the critical current is large enough, an odd number of  $\pi$  junctions within a loop generates a spontaneous orbital moment associated with the circulation current around the loop [21, 22]. The interaction of these orbital moments can lead to ferromagnetic-like ordering (orbital ferromagnetism) [21]. Since the diameter of nanotubes is comparable to the magnetic penetration depth [10], the diamagnetic Meissner effect is negligibly small so that magnetic field can enter into the Josephson-coupled network even in a zero-field-cooled condition. Because the Josephson-coupled loops in MWNT mats should be much smaller than those in the network made of conventional superconductors or cuprate superconductors and because orbital moments are inversely proportional to loop areas [21], the orbital moments in MWNT mats should be significantly larger. Since  $\pi$  junctions can be formed even if the impurities are not in the ferromagnetic state [20], the ferromagnetic-like ordering of the orbital moments can occur above the Curie temperature of the magnetic impurities. This can explain the data shown in Fig. 3a. On the other hand, if the Josephson coupling and critical current are sub-

stantially reduced by the removal of the outershells of MWNTs after annealing in air at 480 °C, the density of the  $\pi$  junctions and thus the orbital moments are significantly reduced above  $T_C$  of the magnetic impurities. However, ferromagnetic ordering of magnetic impurities below  $T_C$  can greatly enhance the critical current due to an increase of the pinning force, as seen in conventional superconductors [23]. This will sharply increase both the density of the  $\pi$  junctions and the orbital moments just below  $T_C$ . This picture can naturally explain the result in Fig. 3b. If this interpretation is correct, our present results imply ultra-high temperature superconductivity in our MWNT mat samples, in agreement with theoretical predictions [14, 15].

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- [1] D. Mendoza, F. Morales, R. Escudero, and J. Walter, *J. Phys.: Condens. Matter* **11**, L317 (1999).
  - [2] Y. Kopelevich, P. Esquinazi, J. H. S. Torres, and S. Moehlecke, *J. Low Temp. Phys.* **119**, 691 (2000).
  - [3] S. Moehlecke, C. Ho, and M. B. Maple, *Phil. Mag. B* **82**, 1335 (2002).
  - [4] K. Murata, H. Ushijima, H. Ueda, and K. Kawaguchi, *J. Chem. Soc. Chem. Commun.* **7**, 567 (1992).
  - [5] T. Makarova, B. Sundqvist, R. Hohne, P. Esquinazi, Y. Kopelevich, P. Scharff, V.A. Davydov, L.S. Kashevarova, and A.V. Rakhmanina, *Nature (London)* **413**, 716 (2001).
  - [6] G. Baskaran and S. A. Jafari, *Phys. Rev. Lett.* **89**, 016402 (2002).
  - [7] A. Dzwilewski, A. Setzer, A. Talyzin, L. Dubrovinsky, P. Esquinazi, *Eur. Phys. J. B* **55**, 57 (2007).
  - [8] K. Antonowicz, *Nature (London)* **247**, 358 (1974).
  - [9] S. G. Lebedev, *Nucl. Instr. Meth.* **A521**, 22 (2004).
  - [10] G. M. Zhao and Y. S. Wang, cond-mat/0111268; G. M. Zhao, *Trends in Nanotubes Research*, edited by Delores A. Martin (Nova Science Publishers, New York, 2006) page 39-75 and references therein.
  - [11] Z. K. Tang, L. Y. Zhang, N. Wang, X. X. Zhang, G. H. Wen, G. D. Li, J. N. Wang, C. T. Chan, and P. Sheng, *Science* **292**, 2462 (2001).
  - [12] I. Takesue, J. Haruyama, N. Kobayashi, S. Chiashi, S. Maruyama, T. Sugai, and H. Shinohara, *Phys. Rev. Lett.* **96**, 057001 (2006).
  - [13] R. Ricardo da Silva, J. H. S. Torres, and Y. Kopelevich, *Phys. Rev. Lett.* **87**, 147001 (2001).
  - [14] J. Gonzalez, F. Guinea, and M. A. H. Vozmediano, *Phys. Rev. B* **63**, 134421 (2001).
  - [15] J. R. Schrieffer, cond-mat/0406200.
  - [16] E. M. Terry, *Phys. Rev.* **XXX**, 133 (1910).
  - [17] The bulk saturation magnetization  $M_s$  of Co at 1100 K is calculated to be 125 emu/g from the value (162 emu/g)

- of  $M_s$  at room temperature and  $T_C = 1404$  K using the temperature dependence of  $M_s$  for Ni; For bulk CoFe,  $M_s$  at 1100 K is 141 emu/g.
- [18] J. M. D. Coey, M. Venkatesan, C. B. Fitzgerald, A. P. Douvalis , and I. S. Sanders, Nature (London) **450**, 156 (2002).
  - [19] J. Restrepo, Y. Labaye, and J.M. Greneche, Physica B **384**, 221 (2006).
  - [20] B. I. Spivak and S. A. Kivelson, Phys. Rev. B **43**, 3740 (1991).
  - [21] F. V. Kusmartsev, Phys. Rev. Lett. **69**, 2268 (1992).
  - [22] D. Dominguez, E. A. Jagla, and C. A. Balserio, Phys. Rev. Lett. **72**, 2773 (1994).
  - [23] N. D. Rizzo, J. Q. Wang, D. E. Probera, L. R. Motowidlo, and B. A. Zeitlin, Appl. Phys. Lett. **69**, 2285 (1996).